

PATENT ABSTRACTS OF JAPAN

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(11)Publication number : 11-073962

(43)Date of publication of application : 16.03.1999

(51)Int.Cl.

H01M 4/58

H01M 4/02

H01M 10/40

(21)Application number : 09-247578

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(22)Date of filing : 29.08.1997

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(54) NONAQUEOUS SYSTEM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous system secondary battery with high voltage, high capacity, superior cycle characteristic, and high storage characteristic and cycle characteristic at high temperature.

SOLUTION: In a nonaqueous system secondary battery having a negative active material capable of absorbing/releasing lithium ions, a positive active material comprising a lithium-containing complex oxide capable of absorbing/ releasing lithium ions, and a lithium ion conductive nonaqueous electrolyte, a spinel lithium manganese complex oxide represented by a general formula $\text{LiXMn}(2-\text{Y}-\text{Z})\text{MYCrZO}(4+\text{P})$ (where M represents Ni or Co, X, Y, Z, P are $0.85 \leq \text{X} \leq 1.2$, $0 < \text{Y} < 0.5$, $0 < \text{Z} < 1$, $2\text{Y} + \text{Z} \leq \text{X}$, and $\text{P} \leq 0$), and having a potential of 4.5 V or higher with respect to Li/Li^+ is used as the positive active material.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application
converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of
rejection][Date of requesting appeal against examiner's decision
of rejection]

[Date of extinction of right]

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(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-73962

(43) 公開日 平成11年(1999) 3月16日

(51) Int.Cl.⁶

識別記号

F I

H 0 1 M 4/58

H 0 1 M 4/58

4/02

4/02

C

10/40

10/40

Z

審査請求 未請求 請求項の数 1 F D (全 6 頁)

(21) 出願番号 特願平9-247578

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(22) 出願日 平成9年(1997) 8月29日

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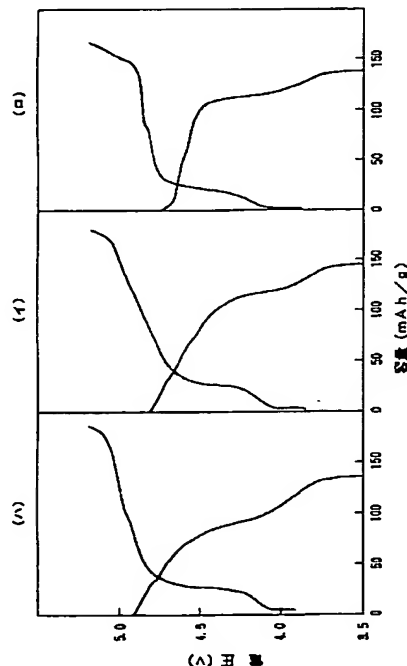
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(54) 【発明の名称】 非水系二次電池

(57) 【要約】

【課題】 高電圧、高容量でサイクル性に優れ、さらに高温での保存およびサイクル性に優れた非水系二次電池を提供することを目的とする。

【解決手段】 リチウムイオンの吸蔵放出が可能な負極活物質と、リチウムイオンの吸蔵放出が可能なリチウム含有複合酸化物からなる正極活物質と、リチウムイオン伝導性の非水電解液を備えた非水系二次電池において、前記正極活物質として、一般式 $Li_x Mn_{(2-Y-Z)} M_Y Cr_2 O_{(4-P)}$ (ただし、MはNiまたはCoを示し、 X, Y, Z, P は各々 $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, $0 < Z < 1$ であかつ $2Y + Z \leq X$, $0 \leq P$ である) で表わされ、 Li/Li^+ に対して4.5V以上の電位を有するスピネル系のリチウムマンガン複合酸化物、を採用することからなる。



【特許請求の範囲】

【請求項1】 リチウムイオンの吸蔵放出が可能な負極活物質と、リチウムイオンの吸蔵放出が可能なリチウム含有複合酸化物からなる正極活物質と、リチウムイオン伝導性の非水電解液を備えた非水系二次電池において、前記リチウム含有複合酸化物が次の一般式 $Li_x Mn_{(2-Y-Z)} M_Y Cr_Z O_{(4+P)}$ (ただし、MはNiまたはCoを示し、X、Y、Z、Pは各々 $0.85 \leq X \leq 1.2$ 、 $0 < Y < 0.5$ 、 $0 < Z < 1$ でかつ $2Y + Z \leq X$ 、 $0 \leq P$ である) で表わされ、 Li/Li^+ に対して4.5V以上の電位を有するスピネル系のリチウムマンガ

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、リチウムマンガ複合酸化物を正極に用いた非水系二次電池に関するものである。

【0002】

【従来の技術】 近年、電子機器の小型化、薄型化、軽量化の傾向は著しく、それに伴い電源となる電池に対しても駆動用、バックアップ用を問わず小型化、薄型化、軽量化かつ、高エネルギー密度化の要求が高まっている。機器の小型化、軽量化が可能なることからリチウムイオン二次電池は、最近携帯電話やノート型パーソナルコンピューターなどの携帯機器に広く用いられるようになってきた。

【0003】 現在一般に市販されているリチウムイオン二次電池は、正極活物質にコバルト酸リチウムを、負極活物質に炭素が用いられている。しかし、正極活物質のコバルト酸リチウムは、コバルトが高価である上、埋蔵量が少ないことから将来供給不足になる可能性がある。これに対し最近、安価で、埋蔵量が豊富な上、コバルト酸リチウムより重量あたりの容量が大きいニッケル酸リチウムやコバルト酸リチウムと同等の高電圧でのリチウムの吸蔵・放出が可能な正極活物質としてスピネル系のリチウム含有マンガ酸化物が注目され、多くの研究がなされている。しかし、さらに高電圧の正極活物質が開発されれば、より一層の高エネルギー密度化が可能になる。さらには、高容量ではあるが電位が高いためコバルト酸リチウム正極との組み合わせではエネルギー密度が低くなってしまふ金属酸化物や、低温焼成炭素材料も負極に用いることも可能になる。このような目的で、スピネル系マンガ酸リチウムのマンガの一部をニッケルで置き換えることが検討されている(ジャーナル・オブ・エレクトロケミカルソサイティー1994年、141巻、2279頁)が、その電圧は4.6-4.7Vで、必ずしも十分とはいえない。

【0004】

【発明が解決しようとする課題】 本発明は、高電圧、高容量でサイクル性に優れ、さらに高温での保存およびサ

イクル性に優れた非水系二次電池を提供することを目的とする。

【0005】

【課題を解決するための手段】 本発明者らが鋭意検討した結果、スピネル系のリチウムマンガ複合酸化物の一部をクロムおよびニッケルまたはコバルトで置換したニッケル、クロム含有マンガ酸リチウムあるいは、コバルト、クロム含有マンガ酸リチウムが金属リチウムに対し約4.8Vの高電圧を有し、かつサイクル特性が優れていることを見いだし本発明を完成するに至った。

【0006】 すなわち本発明は、リチウムイオンの吸蔵放出が可能な負極活物質と、リチウムイオンの吸蔵放出が可能なリチウム含有複合酸化物からなる正極活物質と、リチウムイオン伝導性の非水電解液を備えた非水系二次電池において、前記リチウム含有複合酸化物が次の一般式 $Li_x Mn_{(2-Y-Z)} M_Y Cr_Z O_{(4+P)}$ (ただし、MはNiまたはCoを示し、X、Y、Z、Pは各々 $0.85 \leq X \leq 1.2$ 、 $0 < Y < 0.5$ 、 $0 < Z < 1$ でかつ $2Y + Z \leq X$ 、 $0 \leq P$ である) で表わされ、 Li/Li^+ に対して4.5V以上の電位を有するスピネル系のリチウムマンガ複合酸化物であることを特徴とする非水系二次電池である。

【0007】 以下本発明につき詳細に説明する。本発明は、正極活物質としてのリチウム含有複合酸化物が、次の一般式 $Li_x Mn_{(2-Y-Z)} M_Y Cr_Z O_{(4+P)}$ (ただし、MはNiまたはCoを示し、X、Y、Z、Pは各々 $0.85 \leq X \leq 1.2$ 、 $0 < Y < 0.5$ 、 $0 < Z < 1$ でかつ $2Y + Z \leq X$ 、 $0 \leq P$ である) で表わされ、 Li/Li^+ に対して4.5V以上の電位を有するスピネル系のリチウムマンガ複合酸化物であることを特徴とする非水系二次電池である。 $LiMn_2O_4$ であらわされるスピネル構造のリチウムマンガ複合酸化物の放電電位は、3V付近と4V付近に現れ、通常非水系二次電池正極としては4V領域が利用され、その容量は120mAh/g程度である。

【0008】 一方、 $LiMn_2O_4$ のマンガの一部をニッケルで置換した $LiMn_{1-x}Ni_xO_4$ では、高電位プラトーが4.4-4.7Vにあらわれ、サイクル特性は良好であるが、放電電位はまだ不十分である。また、マンガの一部をクロムで置換した $LiMn_{1-x}Cr_xO_4$ は、高電位プラトーが4.9V-4.5Vにあらわれ、より一層の高電圧化が可能であるが、サイクル特性が悪い。そこで、本発明者らはマンガの一部をニッケルとクロムの両方で置換すると、高電位でかつサイクル特性に優れた正極材料が得られることを見いだした。さらには、ニッケルとコバルトの両方で置換しても同様の効果が得られることを見いだした。

【0009】 このようにマンガの一部を他の金属元素で置換することによってこのような効果が得られる理由は明確ではないが、置換元素の4.5V以上の電圧での

酸化還元が安定的に行なわれ(Ni、Coの2+から4+、Crの3+から4+)、かつ結晶構造の安定化が図られていると考えられる。本発明の上記スピネル系のリチウムマンガン複合酸化物は、好ましくは上記X、Y、Zの値が次の範囲のものである。

1. $0.0 \leq X \leq 1.15$

0. $0.5 \leq Y \leq 0.4$

0. $4 \leq Z < 0.8$

【0010】本発明の上記スピネル系のリチウムマンガン複合酸化物を合成するためのマンガン化合物としては、電解二酸化マンガン、化学合成二酸化マンガン、 γ -MnOOH、炭酸マンガン、硝酸マンガン等が用いられ、リチウム化合物としては、炭酸リチウム、水酸化リチウム、硝酸リチウム、酢酸リチウム等が用いられ、そしてニッケル、コバルト、クロムの化合物としては、それぞれの酸化物、塩化物、硝酸塩、炭酸塩等を用いることができる。

【0011】その際の加熱処理温度は、650℃～900℃が好ましく、さらには750℃～900℃がより好ましく、加熱雰囲気は、空気中あるいは酸素雰囲気下、または窒素雰囲気下が好ましい。本発明の上記スピネル系のリチウムマンガン複合酸化物を合成する方法は、Li原子数がXモルとなる量のリチウム化合物と、マンガン原子数が(2-Y-Z)モルとなる量のマンガン化合物と、ニッケル原子数がYモルとなる量のニッケル化合物、又はコバルト原子数がYモルとなる量のコバルト化合物と、クロム原子数がZモルとなる量のクロム化合物とを混合し、上記温度及び雰囲気中で加熱することからなる。

【0012】本発明のスピネル系リチウムマンガン複合酸化物よりなる正極活物質と組み合わせて用いられる負極活物質としては、通常この種の非水電解質二次電池に用いられる材料がいずれも使用可能で、例えば金属リチウム、リチウム合金、TiO₂、SnSiO₃などの金属酸化物、LiCoN₂等の金属窒化物、炭素材料などを用いることができる。炭素材料としてはコークス、天然黒鉛、人造黒鉛、難黒鉛化炭素等を用いることができる。また、負極活物質としては高容量ではあるが、電位が高いため現行のコバルト酸リチウム正極との組み合わせではエネルギー密度が低くなってしまいう金属酸化物や、低温焼成炭素材料も不都合なく用いることができる。

【0013】電解液としては、リチウム塩を電解質とし、非水溶媒に溶解したものを使用できる。電解質としては、LiClO₄、LiAsF₆、LiPF₆、LiBF₄、LiCF₃SO₃、Li(CF₃SO₂)₂Nなどを単独もしくは2種類以上を混合して用いることができる。有機溶媒としては、特に限定されないが、カーボネート類、ラクトン類、エーテル類などが挙げられ、例えばエチレンカーボネート、プロピレンカーボネート、ジエチルカーボネート、ジメチルカーボネート、メ

チルエチルカーボネート、1,2-ジメトキシエタン、1,2-ジエトキシエタン、テトラヒドロフラン、1,3-ジオキソラン、 γ -ブチロラクトンなどの溶媒を単独もしくは2種類以上を混合して用いることができる。これらの溶媒に溶解される電解質の濃度は0.5～2.0モル/リットルで用いることができる。

【0014】上記の他に、上記電解質を高分子マトリックスに均一分散させた固体または粘稠体、あるいはこれらに非水溶媒を含浸させたものを用いることができる。高分子マトリックスとしては、例えばポリエチレンオキシド、ポリプロピレンオキシド、ポリアクリロニトリル、ポリフッ化ビニリデンなどを用いることができる。また正極と負極の短絡防止のためのセパレーターとしては、ポリエチレン、ポリプロピレン、セルロースなどの材料の多孔性シート、不織布等が用いられる。

【0015】

【発明の実施の形態】以下、本発明の実施の形態を詳細に説明する。

【実施例】

20 (実施例1) 正極活物質の合成は以下の手順で行った。硝酸マンガン、硝酸ニッケルと硝酸クロムをMn、Ni、Crの原子数が各々(2-Y-Z)=1.4モル、Y=0.2モル、Z=0.4モルとなるような割合で秤取り混合し、精製水を加え硝酸水溶液を作った。次にLi原子数(X)が1.0モルとなる量の水酸化リチウムと充分量のアンモニア水を加え、混合し沈殿を作った。その沈殿物を100℃で加熱し、次いで硝酸アンモニウムを除去するために、150℃で加熱、さらに450℃で加熱した。

30 【0016】最後に空气中750℃12時間加熱処理を行うことによって、リチウム含有複合酸化物を得た。得られた生成物は、X線回折と化学分析によりスピネル系構造のLiMn_{1.4}Ni_{0.2}Cr_{0.4}O₄であった。このリチウムマンガン複合酸化物100重量部に対し、導電剤としてアセチレンブラック3重量部と鱗片状黒鉛3重量部を混合した後に、総重量に対し3重量部の割合でN-メチルピロリドン(NMP)を添加して湿式混合を行いペーストとした。次いでこのペーストを正極集電体である厚さ20μmのアルミ箔の両面に均一に塗布し乾燥させた後、150℃に加熱したローラープレス機で加

40 圧成形して帯状の正極を得た。

【0017】正極と負極としての金属リチウムを25μm厚のポリエチレン微多孔膜のセパレータを介して対向させ、三極式のガラスセルに組み、1.0モル/リットルのLiPF₆を溶解したエチレンカーボネート(EC)とジメチルカーボネート(DMC)の混合溶液(容量比1:2)を注入し、充放電容量とサイクル性の測定に供した。次いで、黒鉛化メソカーボン繊維95重量部と鱗片状黒鉛5重量部の混合物に、カルボキシメチルセルロース1重量部とスチレンブタジエンゴム2重量部、溶剤として精製水を添加して湿式混合を行いペーストと

した。このペーストを負極集電体である厚さ12 μ mの銅箔の両面に均一に塗布し、乾燥させた後加圧成形して帯状の負極を作製した。

【0018】上記帯状正極と上記帯状負極の間にセパレーターとして25 μ mの厚さのポリエチレン微多孔膜を挟んでロール状に巻いて捲回体とした。鉄製の角形缶の底部に絶縁性のフィルムを挿入し、前記捲回体を押し潰して挿入した。次いで捲回体から取り出した負極タブを閉塞蓋体に、正極タブを閉塞蓋体の正極ピンに各々溶接した。電池缶の中にエチレンカーボネートとジメチルカーボネートの1:2の混合溶媒に1モル/リットルの濃度でLiPF₆を溶解した電解液を注液した後、閉塞蓋体を溶接し、厚さ8.6mm、巾34mm、高さ48mmの角形電池を作製し、高温特性試験に供した。

【0019】(実施例2) 実施例1と同様の方法でLiMn_{1.2}Ni_{0.2}Cr_{0.5}O₄を合成した。得られたリチウムマンガン複合酸化物を用いて実施例1と同様に電池を作製した。

(実施例3) 実施例1と同様の方法でLi_{1.1}Mn_{1.1}Ni_{0.1}Cr_{0.7}O₄を合成した。得られたリチウムマンガン複合酸化物を用いて実施例1と同様に電池を作製した。

【0020】(実施例4) マンガン化合物として電解二酸化マンガン、リチウム化合物としてLiOH、コバルト化合物として硝酸コバルト、クロム化合物として硝酸クロムを用い、Mn、Li、Co、Crの原子数が各々(2-Y-Z)=1.4モル、X=1.0、Y=0.2モル、Z=0.4モルとなるような割合で秤取り混合し、これを空气中で850℃で24時間加熱処理してLiMn_{1.4}Co_{0.4}Cr_{0.4}O₄を得た。得られたリチウムマンガン複合酸化物を用いて実施例1と同様に電池を作製した。

【0021】(実施例5) 実施例1と同様の方法でLi_{1.1}Mn_{1.4}Co_{0.05}Cr_{0.4}O₄を合成した。得られたリチウムマンガン複合酸化物を用いて実施例1と同様に電池を作製した。

(実施例6) 実施例1と同様の方法でLi_{1.1}Mn_{1.45}Co_{0.05}Cr_{0.4}O₄を合成した。

【0022】得られたリチウムマンガン複合酸化物を用いて、電解液にエチレンカーボネートとジメチルカーボネートの1:2の混合溶媒に1モル/リットルの濃度でLiBF₄を溶解したものを使用した以外は実施例1と同様に電池を作製した。

(比較例1) 実施例1と同様の方法で、LiMn_{1.4}Ni_{0.4}O₄を合成した。得られたリチウムマンガン複合酸化物を用いて実施例1と同様に電池を作製した。

【0023】(比較例2) 実施例1と同様の方法で、LiMn_{1.2}Cr_{0.5}O₄を合成した。得られたリチウムマンガン複合酸化物を用いて実施例1と同様に電池を作製した。

(比較例3) 電解二酸化マンガン、Li₂CO₃および

硝酸クロムを用い、空气中900℃24hr加熱処理してLiMn_{1.4}Cr_{0.5}O₄を合成した。得られたリチウムマンガン複合酸化物を用いて実施例1と同様に電池を作製した。

【0024】(比較例4) 実施例1と同様の方法でLi_{1.0}Mn_{1.95}Co_{0.1}O₄を合成した。得られたリチウムマンガン複合酸化物を用いて、電解液にエチレンカーボネートとジメチルカーボネートの1:2の混合溶媒に1モル/リットルの濃度でLiBF₄を溶解したものを使用した以外は実施例1と同様に電池を作製した。

(試験結果) 実施例及び比較例で作製した電池を以下のように評価した。充電電圧5.2Vで5時間充電を行った後、放電レート0.3Cの電流で3.5Vまで放電を行い、1グラム当たりの容量を求めた。さらに室温(25℃)で、上記の充放電条件でサイクル試験を行った。

【0025】実施例1及び比較例1~2の放電曲線及びサイクル特性(25℃)は、図1(イ)~(ハ)(右上がりの曲線は充電曲線、右下がりの曲線は放電曲線である。)及び図2に示されている。図1~図2に示すとおり、本発明の非水系二次電池は、次の一般式Li_xMn_(2-Y-Z)M_YCr_ZO_(4-P)(ただし、MはNiまたはCoを示し、X、Y、Z、Pは各々0.85≤X≤1.2、0<Y<0.5、0<Z<1でかつ2Y+Z≤X、0≤Pである)で表わされ、Li/Li⁺に対して4.5V以上の電位を有するスピネル系のリチウムマンガン複合酸化物を正極活物質に用いることにより、高電圧、高容量でサイクル性に優れていることが判る。

【0026】(試験結果) さらに、高温特性評価用の電池を充電電圧5.2Vで5時間充電を行った後、放電レート0.5Cで3.5Vまで放電を行い電池容量を求めた。続いてこの充放電サイクルを5サイクル繰り返した後、5.2Vの充電状態で85℃下、120時間保存後、室温まで冷却し放電を行った。自己放電率は(1-(6サイクル目の放電容量/5サイクル目の放電容量))×100により求めた。また、同時に作製した別のセルを用い、充電電圧5.2Vで5時間充電を行った後、放電レート0.5Cで3.5Vまで放電を行うサイクルを60℃下、100サイクル行い、1サイクル目の放電容量に対する100サイクル目の放電容量の比を求め、60℃でのサイクル維持率とした。

【0027】この高温での保存とサイクルの試験の結果は、表1に示されている。表1に示すとおり、本発明の非水系二次電池は、高温での保存およびサイクル性も優れていることが判る。

【0028】

【表1】

表 1

	60℃サイクル 容量維持率 (%)	85℃120時間保存 自己放電率 (%)
実施例1	80	25
実施例2	81	30
実施例3	85	15
実施例4	87	18
実施例5	85	20
実施例6	85	25
比較例1	78	50
比較例2	30	65
比較例3	40	80
比較例4	55	40

【0029】

【発明の効果】以上述べたように、本発明は次の一般式
 $\text{Li}_x\text{Mn}_{(2-Y-Z)}\text{M}_Y\text{Cr}_Z\text{O}_{(4+P)}$ （ただし、Mは*

*NiまたはCoを示し、 X, Y, Z, P は各々 $0.85 \leq X \leq 1.2, 0 < Y < 0.5, 0 < Z < 1$ でかつ $2Y + Z \leq X, 0 \leq P$ である）で表わされ、 Li/Li^+ に対して4.5V以上の電位を有するスピネル系のリチウムマンガ複合酸化物を正極活物質に用いることにより、高電圧、高容量でサイクル性に優れ、さらに高温での保存およびサイクル性にも優れた非水系二次電池を得ることができ、より高エネルギー密度の電池を提供できることからその工業的価値は非常に大きい。

10 【図面の簡単な説明】

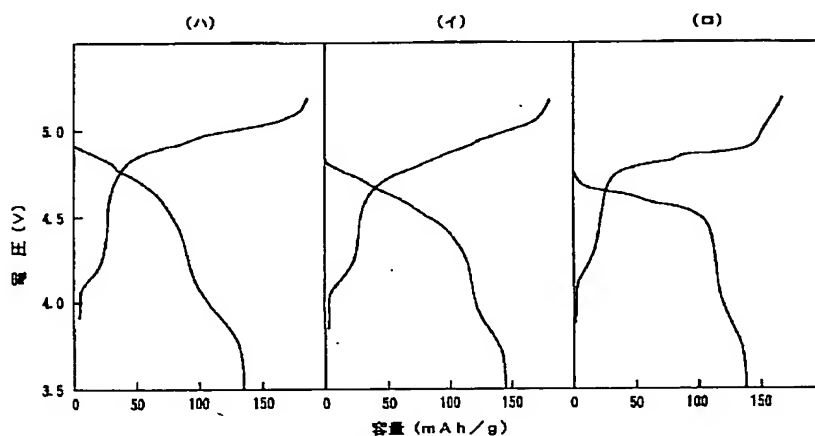
【図1】（イ）実施例1の $\text{LiMn}_{1.4}\text{Cr}_{0.4}\text{Ni}_{0.2}\text{O}_4$ の放電曲線を示す図である。

（ロ）比較例1の $\text{LiMn}_{1.6}\text{Ni}_{0.4}\text{O}_4$ の放電曲線を示す図である。

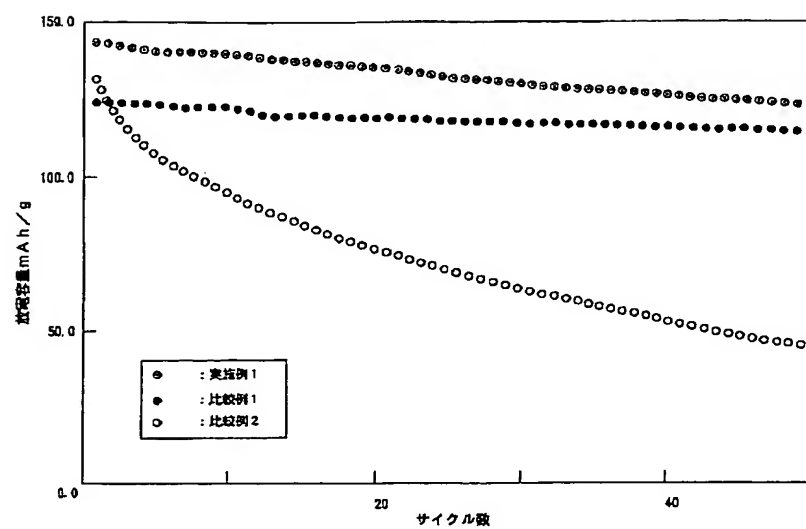
（ハ）比較例2の $\text{LiMn}_{1.2}\text{Cr}_{0.8}\text{O}_4$ の放電曲線を示す図である。

【図2】実施例1及び比較例1～2の電池のサイクル性（1グラム当たりの放電容量）を示す図である。

【図1】



〔図2〕



JAPANESE

[JP,11-073962,A]

AB

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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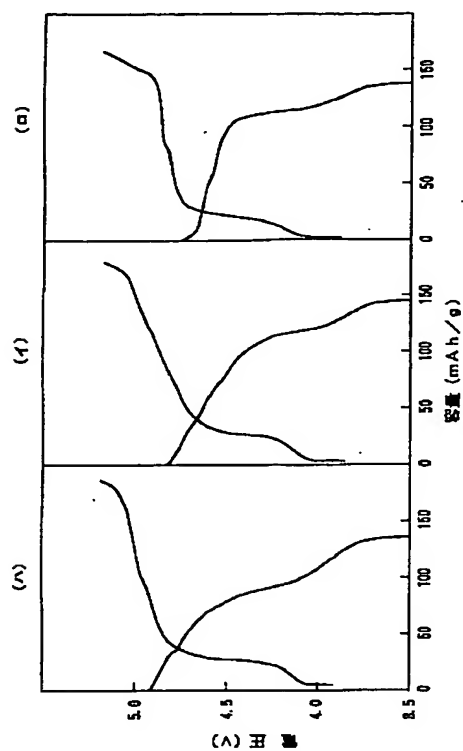
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 CLAIMS

[Claim(s)]

[Claim 1] The negative-electrode active material in which occlusion discharge of a lithium ion is possible. The positive active material which consists of a lithium content multiple oxide in which occlusion discharge of a lithium ion is possible. Nonaqueous electrolyte of lithium ion conductivity. It is the non-drainage system rechargeable battery equipped with the above. the aforementioned lithium content multiple oxide The following general formula $\text{Li}_x \text{Mn}_{(2-Y-Z)} \text{MY} \text{CrZ} \text{O}_{(4+P)}$ however, M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, and $0 < Z < 1$ -- and $2Y + Z \leq X$ -- $0 \leq P$ it is -- it expresses -- having -- Li/Li^+ It is characterized by being the lithium manganese multiple oxide of the spinel system which receives and has the potential beyond 4.5V.

[Translation done.]

Drawing selection ☒ [Representative drawing]

[Translation done.]

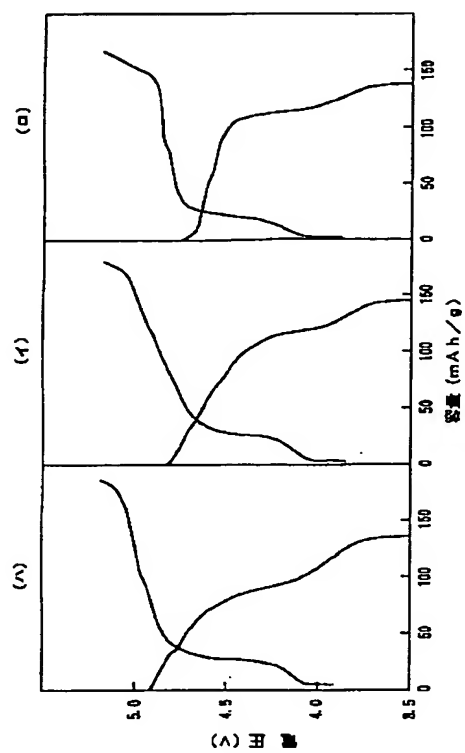
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[JP,11-073962,A]

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[Translation done.]

Drawing selection ☐ [Representative drawing] ☒

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the non-drainage system rechargeable battery which used the lithium manganese multiple oxide for the positive electrode.

[0002]

[Description of the Prior Art] In recent years, the inclination of the miniaturization of electronic equipment, thin-shape-izing, and lightweight-izing is remarkable, and the demand of a miniaturization, thin-shape-izing, lightweight-izing, and the formation of high-energy density is increasing regardless of the object for a drive, and the object for backup also to the cell which serves as a power supply in connection with it. Since the miniaturization of a device and lightweight-izing are possible, a rechargeable lithium-ion battery has come to be widely used for pocket devices, such as a cellular phone and a note type personal computer, recently.

[0003] As for the rechargeable lithium-ion battery marketed by general present, carbon is used for the negative-electrode active material in the cobalt acid lithium at the positive active material. However, the top where cobalt is expensive, since there are few deposits, the cobalt acid lithium of a positive active material may become short supply in the future. On the other hand, it is cheap, and the top with abundant deposits, the lithium content manganic acid ghost of a spinel system attracts attention as a positive active material in which the occlusion and discharge of the lithium in the high voltage equivalent to a nickel acid lithium with a larger capacity per weight than a cobalt acid lithium or a cobalt acid lithium are possible, and many researches are made recently. However, if the positive active material of the high voltage is developed further, much more high-energy density-ization will be attained. Furthermore, although it is high capacity, since potential is high, in combination with a cobalt acid lithium positive electrode, it also becomes possible low-temperature baked-carbon material and to use [the metallic oxide to which an energy density becomes low, and] for a negative electrode. replacing some manganese of a spinel system manganic acid lithium with nickel is considered by such purpose -- **** (journal OBU electrochemical SOSAI tea 1994, 141 volumes, 2279 pages) -- the voltage -- 4.6-4.7V -- it is -- not necessarily -- enough -- **** -- it cannot say

[0004]

[Problem(s) to be Solved by the Invention] this invention aims at offering the non-drainage system rechargeable battery which was excellent in the high voltage and high capacity at cycle nature, and was excellent in the preservation further in an elevated temperature, and cycle nature.

[0005]

[Means for Solving the Problem] As a result of this invention persons' inquiring wholeheartedly, it finds out that the nickel which replaced a part of lithium manganese multiple oxide of a spinel system with chromium and nickel, or cobalt, a chromium content manganic acid lithium or cobalt, and a chromium content manganic acid lithium have the high voltage of about 4.8 V to a metal lithium, and the cycle property is excellent, and came to complete this invention.

[0006] Namely, the negative-electrode active material which this invention can occlusion emit [of a lithium ion], In the non-drainage system rechargeable battery equipped with the positive active material which consists of a lithium content multiple oxide in which occlusion discharge of a lithium ion is possible, and the nonaqueous electrolyte of lithium ion conductivity The aforementioned lithium content multiple oxide The following general formula $\text{LiX Mn (2-Y-Z) MY CrZ O (4+P)}$ however, M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, and $0 < Z < 1$ -- and $2Y+Z \leq X$ -- $0 \leq P$ it is -- it expresses -- having -- Li/Li+ It is the non-drainage system rechargeable battery characterized by being the lithium manganese multiple oxide of the spinel system which receives and has the potential beyond 4.5V.

[0007] It explains to a detail per this invention below. The lithium content multiple oxide as a positive active material this invention The following general formula $\text{LiXMn (2-Y-Z) MY CrZ O (4+P)}$ however, M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, and $0 < Z < 1$ -- and $2Y+Z \leq X$ -- $0 \leq P$ it is -

- it expresses -- having -- Li/Li+ It is the non-drainage system rechargeable battery characterized by being the lithium manganese multiple oxide of the spinel system which receives and has the potential beyond 4.5V. LiMn₂O₄ The discharge potential of the lithium manganese multiple oxide of the Spinel structure expressed appears in the 3V neighborhood and the 4V neighborhood, 4V field is usually used as a non-drainage system rechargeable battery positive electrode, and the capacity is about 120 mAh/g.

[0008] on the other hand -- LiMn₂O₄ LiMn_{1.6}Ni_{0.4}O₄ which replaced some manganese with nickel **** -- although a high potential plateau appears in 4.4-4.7V and the cycle property is good, the discharge potential is still inadequate Moreover, LiMn_{1.2}Cr_{0.8}O₄ which replaced some manganese with chromium A cycle property is bad, although a high potential plateau appears in 4.9V-4.5V and much more high-voltage-izing is possible. Then, when this invention persons replaced some manganese with both nickel and chromium, they found out that the positive-electrode material which is high potential and is excellent in a cycle property was obtained. Furthermore, even if replaced with both nickel and cobalt, it found out that the same effect was acquired.

[0009] Thus, although the reason such an effect is acquired by replacing some manganese by other metallic elements is not clear, oxidation reduction in the voltage beyond 4.5V of a substitution element is performed stably (from 2+ to 4+ of nickel and Co, from 3+ to 4+ of Cr), and it is thought that stabilization of the crystal structure is attained. The lithium manganese multiple oxide of the above-mentioned spinel system of this invention is Above X and Y and Z preferably. A value is the thing of the following range.

$1.00 \leq X \leq 1.15$, $0.05 \leq Y \leq 0.40$, $0.4 \leq Z < 0.8$ [0010] As a manganese compound for compounding the lithium manganese multiple oxide of the above-mentioned spinel system of this invention, an electrolytic manganese dioxide, chemosynthesis manganese dioxide, gamma-MnOOH, manganese carbonate, manganese nitrate, etc. are used, and a lithium carbonate, a lithium hydroxide, a lithium nitrate, an acetic-acid lithium, etc. are used as a lithium compound, and each oxide, a chloride, a nitrate, a carbonate, etc. can be used as a compound of nickel, cobalt, and chromium.

[0011] The heat-treatment temperature in that case has 650 degrees C - desirable 900 degrees C, 750 more degrees C - 900 degrees C are more desirable, and heating atmosphere has the inside of air, or the desirable bottom of oxygen atmosphere or nitrogen-gas-atmosphere mind. The method of compounding the lithium manganese multiple oxide of the above-mentioned spinel system of this invention Li atomic number is X. The lithium compound and manganese atomic number of the amount used as a mol (2-Y-Z) The manganese compound of the amount used as a mol, A nickel atomic number is Y. The nickel compound or cobalt atomic number of the amount used as a mol is Y. The cobalt compound and chromium atomic number of the amount used as a mol are Z. The chromium compound of the amount used as a mol is mixed, and it consists of heating in the above-mentioned temperature and atmosphere.

[0012] the material usually used for this kind of nonaqueous electrolyte rechargeable battery as a negative-electrode active material used combining the positive active material which consists of a spinel system lithium manganese multiple oxide of this invention -- each -- usable -- for example, a metal lithium, a lithium alloy, TiO₂, and SnSiO₃ etc. -- a metallic oxide and LiCoN₂ etc. -- a metal nitride, a carbon material, etc. can be used As a carbon material, corks, a natural graphite, an artificial graphite, difficulty graphitized carbon, etc. can be used. Moreover, although it is high capacity as a negative-electrode active material, since potential is high, in combination with the present cobalt acid lithium positive electrode, the metallic oxide to which an energy density becomes low, and low-temperature baked-carbon material can also be used that there is nothing inconvenient.

[0013] As the electrolytic solution, lithium salt is used as an electrolyte and what was dissolved in the non-aqueous solvent can be used. As an electrolyte, independent or two kinds or more can be mixed, and LiClO₄, LiAsF₆, LiPF₆, LiBF₄, LiCF₃SO₃, Li(CF₃SO₂)₂N, etc. can be used. Especially as an organic solvent, although not limited, carbonate, lactone, ether, etc. are mentioned, for example, independent or two kinds or more can be mixed, and solvents, such as ethylene carbonate, propylene carbonate, diethyl carbonate, dimethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, a tetrahydrofuran, 1, 3-dioxolane, and gamma-butyrolactone, can be used. The concentration of the electrolyte dissolved in these solvents can be used by l. in 0.5-2.0 mols /.

[0014] The solid-state which made the macromolecule matrix carry out uniform distribution of the above-mentioned electrolyte other than the above, a viscous object, or the thing which infiltrated the non-aqueous solvent into these can be used. As a macromolecule matrix, a polyethylene oxide, a polypropylene oxide, a polyacrylonitrile, a polyvinylidene fluoride, etc. can be used, for example. Moreover, as a separator for short circuit prevention of a positive electrode and a negative electrode, the porous sheet of material, such as polyethylene, polypropylene, and a cellulose, a nonwoven fabric, etc. are used.

[0015]
[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained in detail.

[Example]

(Example 1) The following procedures performed composition of a positive active material. The atomic number of

Mn, nickel, and Cr is manganese nitrate, nickel nitrate, and a chromium nitrate respectively (2-Y-Z) = 1.4 Mol Y = 0.2 A mol and Z = 0.4 ***** mixture was carried out at a rate which serves as a mol, the purified water was added, and nitric-acid solution was made. Next, Li atomic number (X) 1.0 The aqueous ammonia of an amount was enough added with the lithium hydroxide of the amount used as a mol, it mixed, and precipitation was made. In order to heat the precipitate at 100 degrees C and to remove an ammonium nitrate subsequently, it heated at heating and 450 more degrees C by 150 degrees C.

[0016] The lithium content multiple oxide was obtained by finally performing heat-treatment for 750-degree-C 12 hours in air. the obtained product -- an X diffraction and a chemical analysis -- $\text{LiMn}_{1.4}\text{Ni}_{0.2}\text{Cr}_{0.4}\text{O}_4$ of spinel system structure it was . After mixing the acetylene black 3 weight section and the scale-like graphite 3 weight section as an electric conduction agent to this lithium manganese multiple-oxide 100 weight section, N-methyl pyrrolidone (NMP) was added at a rate of 3 weight sections to AUW, wet blending was performed, and it considered as the paste. Subsequently, after applying this paste to both sides of aluminum foil with a thickness of 20 micrometers which is a positive-electrode charge collector uniformly and making them dry it, pressing was carried out with the roller-press machine heated at 150 degrees C, and the band-like positive electrode was obtained.

[0017] The metal lithium as a positive electrode and a negative electrode is made to counter through the separator of the polyethylene fine porous membrane of 25-micrometer **, and it constructs to the glass cell of a trilateral formula, and is 1.0 mols [/l.] LiPF_6 . The mixed solution (capacity factor 1:2) of the ethylene carbonate (EC) which dissolved, and dimethyl carbonate (DMC) was poured in, and measurement of charge-and-discharge capacity and cycle nature was presented. Subsequently, the purified water was added as the carboxymethyl-cellulose 1 weight section, the styrene-butadiene-rubber 2 weight section, and a solvent into the mixture of the graphitization meso carbon-fiber 95 weight section and the scale-like graphite 5 weight section, wet blending was performed, and it considered as the paste. This paste was uniformly applied to both sides of copper foil with a thickness of 12 micrometers which is a negative-electrode charge collector, after making it dry, pressing was carried out and the band-like negative electrode was produced.

[0018] Between the above-mentioned band-like positive electrode and the above-mentioned band-like negative electrode, on both sides of the polyethylene fine porous membrane with a thickness of 25 micrometers, it wound in the shape of a roll as a separator, and considered as the winding object. The insulating film was inserted in the pars basilaris ossis occipitalis of an iron square shape can, and the aforementioned winding object was crushed and inserted. Subsequently, the negative-electrode tab picked out from the winding object was welded to the lock out lid, and the positive-electrode tab was respectively welded to the positive-electrode pin of a lock out lid. It is LiPF_6 at the concentration of one mol/l. to the mixed solvent of 1:2 of ethylene carbonate and dimethyl carbonate in a cell can. After pouring in the electrolytic solution which dissolved, the lock out lid was welded, the square shape cell with the thickness of 8.6mm, a width [of 34mm], and a height of 48mm was produced, and the elevated-temperature characteristic test was presented.

[0019] (Example 2) It is $\text{LiMn}_{1.25}\text{Ni}_{0.25}\text{Cr}_{0.5}\text{O}_4$ with the same method as an example 1. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

(Example 3) It is $\text{Li}_{1.15}\text{Mn}_{1.15}\text{Ni}_{0.1}\text{Cr}_{0.75}\text{O}_4$ with the same method as an example 1. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

[0020] As a manganese compound, as an electrolytic manganese dioxide and a lithium compound LiOH , (Example 4) Are used a cobalt nitrate as a cobalt compound and a chromium nitrate is used as a chromium compound. The atomic number of Mn, Li, Co, and Cr is =1.4 respectively (2-Y-Z). Mol, X = 1.0 and Y = 0.2 A mol and Z = 0.4 ***** mixture is carried out at a rate which serves as a mol, this is heat-treated at 850 degrees C in air for 24 hours, and it is $\text{LiMn}_{1.4}\text{Co}_{0.2}\text{Cr}_{0.4}\text{O}_4$. It obtained. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

[0021] (Example 5) It is $\text{Li}_{1.1}\text{Mn}_{1.45}\text{Co}_{0.05}\text{Cr}_{0.4}\text{O}_4$ with the same method as an example 1. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

(Example 6) It is $\text{Li}_{1.1}\text{Mn}_{1.45}\text{Co}_{0.05}\text{Cr}_{0.4}\text{O}_4$ with the same method as an example 1. It compounded.

[0022] The obtained lithium manganese multiple oxide is used and it is LiBF_4 at the concentration of one mol/l. to the mixed solvent of 1:2 of ethylene carbonate and dimethyl carbonate in the electrolytic solution. The cell was produced like the example 1 except having used what was dissolved.

(Example 1 of comparison) With the same method as an example 1, it is $\text{LiMn}_{1.6}\text{Ni}_{0.4}\text{O}_4$. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

[0023] (Example 2 of comparison) With the same method as an example 1, it is $\text{LiMn}_{1.2}\text{Cr}_{0.8}\text{O}_4$. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

(Example 3 of comparison) An electrolytic manganese dioxide and Li_2CO_3 It reaches, 900-degree-C24hr heat-treatment in air is carried out using a chromium nitrate, and it is $\text{LiMn}_{1.5}\text{Cr}_{0.5}\text{O}_4$. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

[0024] (Example 4 of comparison) It is $\text{Li}_{1.0}\text{Mn}_{1.90}\text{Co}_{0.1}\text{O}_4$ with the same method as an example 1. It

compounded. The obtained lithium manganese multiple oxide is used and it is LiBF_4 at the concentration of one mol/l. to the mixed solvent of 1:2 of ethylene carbonate and dimethyl carbonate in the electrolytic solution. The cell was produced like the example 1 except having used what was dissolved.

(Test result) The cell produced in the example and the example of comparison was evaluated as follows. After performing charge by charge voltage 5.2V for 5 hours, it discharged to 3.5V with the current of electric discharge rate 0.3C, and the capacity per g was calculated. Furthermore, the room temperature (25 degrees C) performed the cycle examination on the above-mentioned charge-and-discharge conditions.

[0025] The discharge curve and cycle property (25 degrees C) of an example 1 and the examples 1-2 of comparison are shown in the drawing 1 (**) - (**) (as for a curve upward slanting to the right, a charging curve and the lower right of the curve of ** are discharge curves.), and drawing 2. As shown in drawing 1 - drawing 2 the non-drainage system rechargeable battery of this invention The following general formula $\text{LiX Mn (2-Y-Z) MY CrZ O (4+P)}$ $Z \leq X$ however, M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, and $0 < Z < 1$ -- and $2Y + Z \leq X$ -- $0 \leq P$ it is -- it expresses -- having -- Li/Li+ By using for a positive active material the lithium manganese multiple oxide of the spinel system which receives and has the potential beyond 4.5V shows excelling in the high voltage and high capacity at cycle nature.

[0026] (Test result) The cell further for elevated-temperature characterization was discharged to 3.5V by electric discharge rate 0.5C, after performing charge by charge voltage 5.2V for 5 hours, and cell capacity was calculated. Then, it discharged by cooling this charge-and-discharge cycle in the state of charge of 5.2V after 5 cycle ***** the bottom of 85 degrees C, after 120-hour preservation, and to a room temperature. It asked for the rate of self-discharge by $\{1 - (\text{amount of electric discharge of amount of electric discharge} / 5 \text{ cycle eye of } 6 \text{ cycle eye})\} \times 100$. Moreover, after performing charge by charge voltage 5.2V for 5 hours using another cell produced simultaneously, it asked for the ratio of the service capacity [as opposed to the service capacity of a 100 cycle deed and 1 cycle eye for the cycle which discharges to 3.5V by electric discharge rate 0.5C] of a 100 cycle eye under 60 degrees C, and considered as the 60-degree C cycle maintenance factor.

[0027] The result of an examination of the preservation in this elevated temperature and a cycle is shown in Table 1. It turns out that the non-drainage system rechargeable battery of this invention is excellent also in the preservation in an elevated temperature, and cycle nature as shown in Table 1.

[0028]

[Table 1]

表 1

	60℃サイクル 容量維持率 (%)	85℃120時間保存 自己放電率 (%)
実施例 1	80	25
実施例 2	81	30
実施例 3	85	15
実施例 4	87	18
実施例 5	85	20
実施例 6	85	25
比較例 1	78	50
比較例 2	30	65
比較例 3	40	80
比較例 4	55	40

[0029]

[Effect of the Invention] As stated above, this invention The following general formula $\text{LiX Mn (2-Y-Z) MY CrZ O (4+P)}$ however, M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, and $0 < Z < 1$ -- and $2Y + Z \leq X$ -- $0 \leq P$ it is -- it expresses -- having -- Li/Li+ By using for a positive active material the lithium manganese multiple oxide of the spinel system which receives and has the potential beyond 4.5V Since the non-drainage system rechargeable battery which was excellent in the high voltage and high capacity at cycle nature, and was excellent also in the preservation further in an elevated temperature and cycle nature can be obtained and the cell of high-energy density can be offered more, the industrial value is very large.

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TECHNICAL FIELD

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PRIOR ART

[Description of the Prior Art] In recent years, the inclination of the miniaturization of electronic equipment, thin-shape-izing, and lightweight-izing is remarkable, and the demand of a miniaturization, thin-shape-izing, lightweight-izing, and the formation of high-energy density is increasing regardless of the object for a drive, and the object for backup also to the cell which serves as a power supply in connection with it. Since the miniaturization of a device and lightweight-izing are possible, a rechargeable lithium-ion battery has come to be widely used for pocket devices, such as a cellular phone and a note type personal computer, recently.

[0003] As for the rechargeable lithium-ion battery marketed by general present, carbon is used for the negative-electrode active material in the cobalt acid lithium at the positive active material. However, the top where cobalt is expensive, since there are few deposits, the cobalt acid lithium of a positive active material may become short supply in the future. On the other hand, it is cheap, and the top with abundant deposits, the lithium content manganic acid ghost of a spinel system attracts attention as a positive active material in which the occlusion and discharge of the lithium in the high voltage equivalent to a nickel acid lithium with a larger capacity per weight than a cobalt acid lithium or a cobalt acid lithium are possible, and many researches are made recently. However, if the positive active material of the high voltage is developed further, much more high-energy density-ization will be attained. Furthermore, although it is high capacity, since potential is high, in combination with a cobalt acid lithium positive electrode, it also becomes possible low-temperature baked-carbon material and to use [the metallic oxide to which an energy density becomes low, and] for a negative electrode. replacing some manganese of a spinel system manganic acid lithium with nickel is considered by such purpose -- **** (journal OBU electrochemical SOSAI tea 1994, 141 volumes, 2279 pages) -- the voltage -- 4.6-4.7V -- it is -- not necessarily -- enough -- **** -- it cannot say

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EFFECT OF THE INVENTION

[Effect of the Invention] As stated above, in this invention The following general formula $\text{LiX Mn (2-Y-Z) MY CrZ O (4+P)}$ however, M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, and $0 < Z < 1$ -- and $2Y+Z \leq X$ -- $0 \leq P$ it is -- it expresses -- having -- Li/Li^+ The lithium manganese multiple oxide of the spinel system which receives and has the potential beyond 4.5V is used for a positive active material. Therefore, since the non-drainage system rechargeable battery which was excellent in the high voltage and high capacity at cycle nature, and was excellent also in the preservation further in an elevated temperature and cycle nature can be obtained and the cell of high-energy density can be offered more, the industrial value is very large.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention aims at offering the non-drainage system rechargeable battery which was excellent in the high voltage and high capacity at cycle nature, and was excellent in the preservation further in an elevated temperature, and cycle nature.

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MEANS

[Means for Solving the Problem] As a result of this invention persons' inquiring wholeheartedly, it finds out that the nickel which replaced a part of lithium manganese multiple oxide of a spinel system with chromium and nickel, or cobalt, a chromium content manganic acid lithium or cobalt, and a chromium content manganic acid lithium have the high voltage of about 4.8 V to a metal lithium, and the cycle property is excellent, and came to complete this invention.

[0006] That is, this invention is a non-drainage system rechargeable battery characterized by being the lithium manganese multiple oxide of the spinel system characterized by providing the following. The negative-electrode active material in which occlusion discharge of a lithium ion is possible. The positive active material which consists of a lithium content multiple oxide in which occlusion discharge of a lithium ion is possible. In the non-drainage system rechargeable battery equipped with the nonaqueous electrolyte of lithium ion conductivity The aforementioned lithium content multiple oxide The following general formula $\text{LiX Mn (2-Y-Z) MY CrZ O (4+P)}$ (however M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$ and $0 < Y < 0.5$ and $0 < Z < 1$ -- and they are $2Y+Z \leq X$ and $0 \leq P$ -- it expresses with) -- having -- Li/Li+ receiving -- potential beyond 4.5V

[0007] It explains to a detail per this invention below. The lithium content multiple oxide as a positive active material this invention The following general formula $\text{LiXMn (2-Y-Z) MY CrZ O (4+P)}$ however, M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, and $0 < Z < 1$ -- and $2Y+Z \leq X$ -- $0 \leq P$ it is -- it expresses -- having -- Li/Li+ It is the non-drainage system rechargeable battery characterized by being the lithium manganese multiple oxide of the spinel system which receives and has the potential beyond 4.5V. LiMn_2O_4 The discharge potential of the lithium manganese multiple oxide of the Spinel structure expressed appears in the 3V neighborhood and the 4V neighborhood, 4V field is usually used as a non-drainage system rechargeable battery positive electrode, and the capacity is about 120 mAh/g.

[0008] on the other hand -- LiMn_2O_4 $\text{LiMn}_{1.6}$ nickel 0.4O_4 which replaced some manganese with nickel **** -- although a high potential plateau appears in 4.4-4.7V and the cycle property is good, the discharge potential is still inadequate Moreover, $\text{LiMn}_{1.2}$ Cr 0.8O_4 which replaced some manganese with chromium A cycle property is bad, although a high potential plateau appears in 4.9V-4.5V and much more high-voltage-izing is possible. Then, when this invention persons replaced some manganese with both nickel and chromium, they found out that the positive-electrode material which is high potential and is excellent in a cycle property was obtained. Furthermore, even if replaced with both nickel and cobalt, it found out that the same effect was acquired.

[0009] Thus, although the reason such an effect is acquired by replacing some manganese by other metallic elements is not clear, oxidation reduction in the voltage beyond 4.5V of a substitution element is performed stably (from 2+ to 4+ of nickel and Co, from 3+ to 4+ of Cr), and it is thought that stabilization of the crystal structure is attained. The lithium manganese multiple oxide of the above-mentioned spinel system of this invention is Above X and Y and Z preferably. A value is the thing of the following range.

$1.00 \leq X \leq 1.15$ $0.05 \leq Y \leq 0.40$ $0.4 \leq Z < 0.8$. [0010] As a manganese compound for compounding the lithium manganese multiple oxide of the above-mentioned spinel system of this invention, an electrolytic manganese dioxide, chemosynthesis manganese dioxide, gamma- MnOOH , manganese carbonate, manganese nitrate, etc. are used, and a lithium carbonate, a lithium hydroxide, a lithium nitrate, an acetic-acid lithium, etc. are used as a lithium compound, and each oxide, a chloride, a nitrate, a carbonate, etc. can be used as a compound of nickel, cobalt, and chromium.

[0011] The heat-treatment temperature in that case has 650 degrees C - desirable 900 degrees C, 750 more degrees C - 900 degrees C are more desirable, and heating atmosphere has the inside of air, or the desirable bottom of oxygen atmosphere or nitrogen-gas-atmosphere mind. this invention is characterized by providing the following in the method of compounding the lithium manganese multiple oxide of the above-mentioned spinel system. Li atomic number is X. Lithium compound of the amount used as a mol. A manganese atomic number (2-Y-Z) Manganese compound of the amount used as a mol. A nickel atomic number is Y. The nickel compound or cobalt atomic number of the amount used as a mol is Y. Cobalt compound of the amount used as a mol. A chromium atomic

number is Z. ** which mixes the chromium compound of the amount used as a mol, and is heated in the above-mentioned temperature and atmosphere.

[0012] the material usually used for this kind of nonaqueous electrolyte rechargeable battery as a negative-electrode active material used combining the positive active material which consists of a spinel system lithium manganese multiple oxide of this invention -- each -- usable -- for example, a metal lithium, a lithium alloy, TiO_2 , and SnSiO_3 etc. -- a metallic oxide and LiCoN_2 etc. -- a metal nitride, a carbon material, etc. can be used As a carbon material, corks, a natural graphite, an artificial graphite, difficulty graphitized carbon, etc. can be used. Moreover, although it is high capacity as a negative-electrode active material, since potential is high, in combination with the present cobalt acid lithium positive electrode, the metallic oxide to which an energy density becomes low, and low-temperature baked-carbon material can also be used that there is nothing inconvenient.

[0013] As the electrolytic solution, lithium salt is used as an electrolyte and what was dissolved in the non-aqueous solvent can be used. As an electrolyte, independent or two kinds or more can be mixed, and LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, etc. can be used. Especially as an organic solvent, although not limited, carbonate, lactone, ether, etc. are mentioned, for example, independent or two kinds or more can be mixed, and solvents, such as ethylene carbonate, propylene carbonate, diethyl carbonate, dimethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, a tetrahydrofuran, 1, 3-dioxolane, and gamma-butyrolactone, can be used. The concentration of the electrolyte dissolved in these solvents can be used by 1. in 0.5-2.0 mols /.

[0014] The solid-state which made the macromolecule matrix carry out uniform distribution of the above-mentioned electrolyte other than the above, a viscous object, or the thing which infiltrated the non-aqueous solvent into these can be used. As a macromolecule matrix, a polyethylene oxide, a polypropylene oxide, a polyacrylonitrile, a polyvinylidene fluoride, etc. can be used, for example. Moreover, as a separator for short circuit prevention of a positive electrode and a negative electrode, the porous sheet of material, such as polyethylene, polypropylene, and a cellulose, a nonwoven fabric, etc. are used.

[0015]
[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained in detail.

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EXAMPLE

[Example]

(Example 1) The following procedures performed composition of a positive active material. The atomic number of Mn, nickel, and Cr is manganese nitrate, nickel nitrate, and a chromium nitrate respectively (2-Y-Z)=1.4 Mol Y=0.2 A mol and Z=0.4 ***** mixture was carried out at a rate which serves as a mol, the purified water was added, and nitric-acid solution was made. Next, Li atomic number (X) 1.0 The aqueous ammonia of an amount was enough added with the lithium hydroxide of the amount used as a mol, it mixed, and precipitation was made. In order to heat the precipitate at 100 degrees C and to remove an ammonium nitrate subsequently, it heated at heating and 450 more degrees C by 150 degrees C.

[0016] The lithium content multiple oxide was obtained by finally performing heat-treatment for 750-degree-C 12 hours in air. the obtained product -- an X diffraction and a chemical analysis -- $\text{LiMn}_{1.4}\text{Ni}_{0.2}\text{Cr}_{0.4}\text{O}_4$ of spinel system structure it was. After mixing the acetylene black 3 weight section and the scale-like graphite 3 weight section as an electric conduction agent to this lithium manganese multiple-oxide 100 weight section, N-methyl pyrrolidone (NMP) was added at a rate of 3 weight sections to AUW, wet blending was performed, and it considered as the paste. Subsequently, after applying this paste to both sides of aluminum foil with a thickness of 20 micrometers which is a positive-electrode charge collector uniformly and making them dry it, pressing was carried out with the roller-press machine heated at 150 degrees C, and the band-like positive electrode was obtained.

[0017] The metal lithium as a positive electrode and a negative electrode is made to counter through the separator of the polyethylene fine porous membrane of 25-micrometer **, and it constructs to the glass cell of a trilateral formula, and is 1.0 mols [/l.] LiPF_6 . The mixed solution (capacity factor 1:2) of the ethylene carbonate (EC) which dissolved, and dimethyl carbonate (DMC) was poured in, and measurement of charge-and-discharge capacity and cycle nature was presented. Subsequently, the purified water was added as the carboxymethyl-cellulose 1 weight section, the styrene-butadiene-rubber 2 weight section, and a solvent into the mixture of the graphitization meso carbon-fiber 95 weight section and the scale-like graphite 5 weight section, wet blending was performed, and it considered as the paste. This paste was uniformly applied to both sides of copper foil with a thickness of 12 micrometers which is a negative-electrode charge collector, after making it dry, pressing was carried out and the band-like negative electrode was produced.

[0018] Between the above-mentioned band-like positive electrode and the above-mentioned band-like negative electrode, on both sides of the polyethylene fine porous membrane with a thickness of 25 micrometers, it wound in the shape of a roll as a separator, and considered as the winding object. The insulating film was inserted in the pars basilaris ossis occipitalis of an iron square shape can, and the aforementioned winding object was crushed and inserted. Subsequently, the negative-electrode tab picked out from the winding object was welded to the lock out lid, and the positive-electrode tab was respectively welded to the positive-electrode pin of a lock out lid. It is LiPF_6 at the concentration of one mol/l. to the mixed solvent of 1:2 of ethylene carbonate and dimethyl carbonate in a cell can. After pouring in the electrolytic solution which dissolved, the lock out lid was welded, the square shape cell with the thickness of 8.6mm, a width [of 34mm], and a height of 48mm was produced, and the elevated-temperature characteristic test was presented.

[0019] (Example 2) It is $\text{LiMn}_{1.25}\text{Ni}_{0.25}\text{Cr}_{0.5}\text{O}_4$ with the same method as an example 1. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

(Example 3) It is $\text{Li}_{1.15}\text{Mn}_{1.15}\text{Ni}_{0.1}\text{Cr}_{0.75}\text{O}_4$ with the same method as an example 1. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

[0020] As a manganese compound, as an electrolytic manganese dioxide and a lithium compound LiOH , (Example 4) Are used a cobalt nitrate as a cobalt compound and a chromium nitrate is used as a chromium compound. The atomic number of Mn, Li, Co, and Cr is =1.4 respectively (2-Y-Z). Mol, X= 1.0 and Y = 0.2 A mol and Z = 0.4 ***** mixture is carried out at a rate which serves as a mol, this is heat-treated at 850 degrees C in air for 24 hours, and it is $\text{LiMn}_{1.4}\text{Co}_{0.2}\text{Cr}_{0.4}\text{O}_4$. It obtained. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

[0021] (Example 5) It is $\text{Li}_{1.1} \text{Mn}_{1.45} \text{Co}_{0.05} \text{Cr}_{0.4} \text{O}_4$ with the same method as an example 1. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

(Example 6) It is $\text{Li}_{1.1} \text{Mn}_{1.45} \text{Co}_{0.05} \text{Cr}_{0.4} \text{O}_4$ with the same method as an example 1. It compounded.

[0022] The obtained lithium manganese multiple oxide is used and it is LiBF_4 at the concentration of one mol/l. to the mixed solvent of 1:2 of ethylene carbonate and dimethyl carbonate in the electrolytic solution. The cell was produced like the example 1 except having used what was dissolved.

(Example 1 of comparison) With the same method as an example 1, it is $\text{LiMn}_{1.6} \text{Ni}_{0.4} \text{O}_4$. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

[0023] (Example 2 of comparison) With the same method as an example 1, it is $\text{LiMn}_{1.2} \text{Cr}_{0.8} \text{O}_4$. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

(Example 3 of comparison) An electrolytic manganese dioxide and $\text{Li}_2 \text{CO}_3$ It reaches, 900-degree-C24hr heat-treatment in air is carried out using a chromium nitrate, and it is $\text{LiMn}_{1.5} \text{Cr}_{0.5} \text{O}_4$. It compounded. The cell was produced like the example 1 using the obtained lithium manganese multiple oxide.

[0024] (Example 4 of comparison) It is $\text{Li}_{1.0} \text{Mn}_{1.90} \text{Co}_{0.1} \text{O}_4$ with the same method as an example 1. It compounded. The obtained lithium manganese multiple oxide is used and it is LiBF_4 at the concentration of one mol/l. to the mixed solvent of 1:2 of ethylene carbonate and dimethyl carbonate in the electrolytic solution. The cell was produced like the example 1 except having used what was dissolved.

(Test result) The cell produced in the example and the example of comparison was evaluated as follows. After performing charge by charge voltage 5.2V for 5 hours, it discharged to 3.5V with the current of electric discharge rate 0.3C, and the capacity per g was calculated. Furthermore, the room temperature (25 degrees C) performed the cycle examination on the above-mentioned charge-and-discharge conditions.

[0025] The discharge curve and cycle property (25 degrees C) of an example 1 and the examples 1-2 of comparison are shown in the drawing 1 (**) - (**) (as for a curve upward slanting to the right, a charging curve and the lower right of the curve of ** are discharge curves.), and drawing 2. As shown in drawing 1 - drawing 2 the non-drainage system rechargeable battery of this invention The following general formula $\text{Li}_x \text{Mn}_{(2-Y-Z)} \text{MY Cr}_Z \text{O}_{(4+P)}$ $Z \leq X$ however, M -- nickel or Co -- being shown -- X, Y, Z, and P -- each $0.85 \leq X \leq 1.2$, $0 < Y < 0.5$, and $0 < Z < 1$ -- and $2Y + 0 \leq P$ it is -- it expresses -- having -- Li/Li^+ By using for a positive active material the lithium manganese multiple oxide of the spinel system which receives and has the potential beyond 4.5V shows excelling in the high voltage and high capacity at cycle nature.

[0026] (Test result) The cell further for elevated-temperature characterization was discharged to 3.5V by electric discharge rate 0.5C, after performing charge by charge voltage 5.2V for 5 hours, and cell capacity was calculated. Then, it discharged by cooling this charge-and-discharge cycle in the state of charge of 5.2V after 5 cycle ***** the bottom of 85 degrees C, after 120-hour preservation, and to a room temperature. It asked for the rate of self-discharge by $\{1 - (\text{amount of electric discharge of amount of electric discharge} / 5 \text{ cycle eye of } 6 \text{ cycle eye})\} \times 100$. Moreover, after performing charge by charge voltage 5.2V for 5 hours using another cell produced simultaneously, it asked for the ratio of the service capacity [as opposed to the service capacity of a 100 cycle deed and 1 cycle eye for the cycle which discharges to 3.5V by electric discharge rate 0.5C] of a 100 cycle eye under 60 degrees C, and considered as the 60-degree C cycle maintenance factor.

[0027] The result of an examination of the preservation in this elevated temperature and a cycle is shown in Table 1. It turns out that the non-drainage system rechargeable battery of this invention is excellent also in the preservation in an elevated temperature, and cycle nature as shown in Table 1.

[0028]

[Table 1]

表 1

	60℃サイクル 容量維持率 (%)	85℃120時間保存 自己放電率 (%)
実施例1	80	25
実施例2	81	30
実施例3	85	15
実施例4	87	18
実施例5	85	20
実施例6	85	25
比較例1	78	50
比較例2	30	65
比較例3	40	80
比較例4	55	40

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] (b) $\text{LiMn}_{1.4}\text{Cr}_{0.4}\text{nickel}_{0.2}\text{O}_4$ of an example 1 It is drawing showing a discharge curve.

(b) $\text{LiMn}_{1.6}\text{nickel}_{0.4}\text{O}_4$ of the example 1 of comparison It is drawing showing a discharge curve.

(c) $\text{LiMn}_{1.2}\text{Cr}_{0.8}\text{O}_4$ of the example 2 of comparison It is drawing showing a discharge curve.

[Drawing 2] It is drawing showing the cycle nature (service capacity per g) of the cell of an example 1 and the examples 1-2 of comparison.

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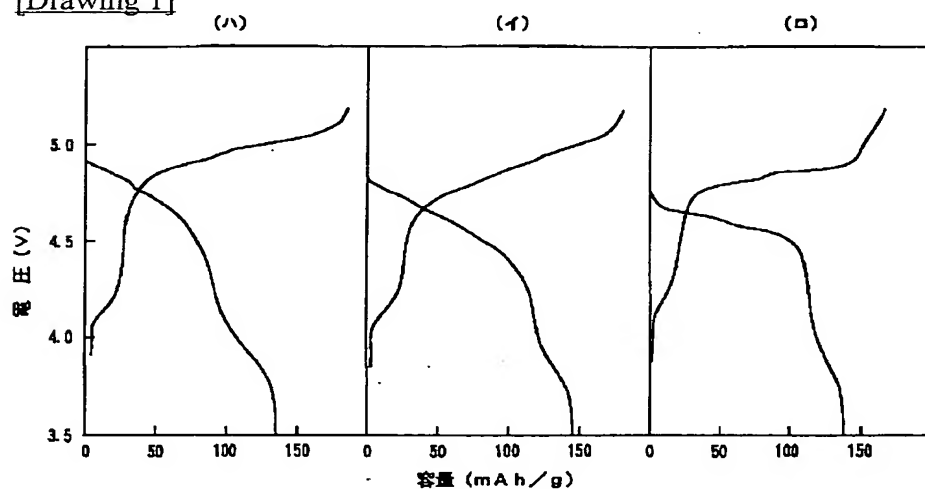
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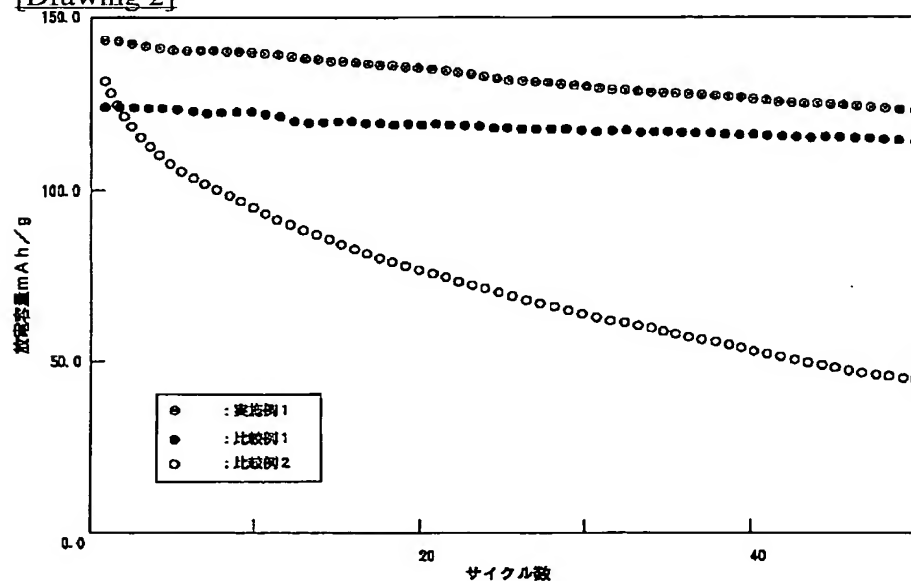
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DRAWINGS

[Drawing 1]



[Drawing 2]



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